

INDENYL TITANIUM(IV) POLYMERIZATION CATALYSTS

An Honors Thesis (HONRS 499)

By

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Thesis Advisor

Dr. Robert J. Morris

A handwritten signature in black ink, appearing to read "Robert J. Morris". The signature is fluid and cursive, with the first name "Robert" being the most prominent part.

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May 2004

Graduation: May 2004

2004
1995

Abstract

The concepts of organometallic chemistry were used to synthesize a new polymerization catalyst. The goal was to create a new compound with a greater efficiency for polymerization, and which does not require expensive and toxic chemicals in order for it to function. Although several different methods were attempted in this project, the only reactions that were reported gave a successful product. In order to monitor the reactions, nuclear magnetic spectroscopy was used as insight into the structure of the compounds.

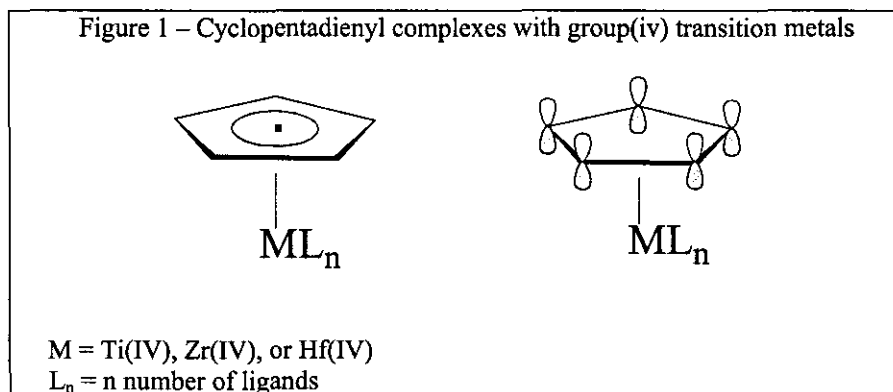
Acknowledgements

- I would like to thank Dr. Robert Morris for advising me through this project. He was very helpful throughout the fellowship, and in checking my paper for errors.

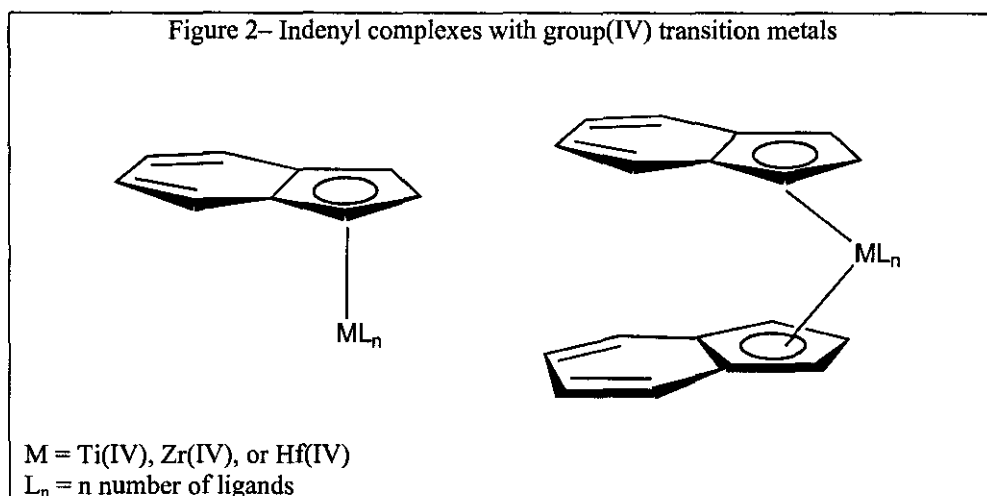
INDENYL TITANIUM (IV) POLYMERIZATION CATALYSTS

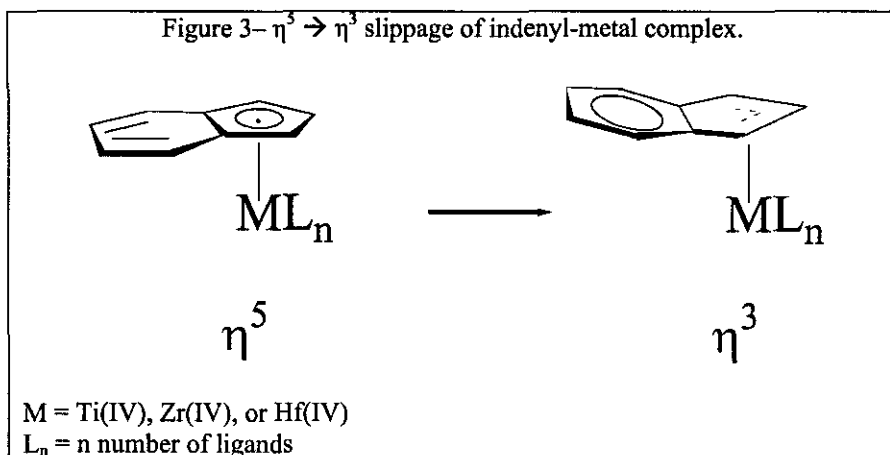
Introduction:

In this project, the concepts of organometallic chemistry were used to synthesize the precursor to a polymerization catalyst. The study of organometallic chemistry involves complexes where carbon-based molecules are bonded to transition metals. Transition metals can form several bonds, and can have up to eighteen electrons occupying the outer, bonding, orbital. Group 4 transition metals like titanium(IV), zirconium(IV) and hafnium(IV) have only 4 electrons of their own to occupy their outer shell, and can therefore form several bonds with other molecules. These metals are known to form a complex with cyclopentadiene which is a five-membered, carbon-based, ring with two double bonds (Figure 1). All five carbons of the ring are involved in the bond to the group 4 metal center; as a result, six additional electrons occupy the outer shell of the titanium(IV). These organometallic compounds are used as catalysts to facilitate the formation of chains of organic compounds by combining molecules with a double bond, olefins, by breaking the bond to form the chain.



In this project, indene, a similar complex to cyclopentadiene, with a six-membered ring sharing a bond with the five-membered ring (Figure 2), was used in complex with titanium(IV). The indenyl compound has diminished interactions between the bridgehead carbons, which link the rings together, and the titanium(IV). In addition, the re-aromatizing of the six-membered ring can cause the indenyl complexes to slip from a bond involving all five carbons in the five-membered ring, η^5 , to a bond involving only the three outer carbons, η^3 (Figure 3). The advantage of this slippage is that the titanium is free to form a fifth bond with the double bond of the olefin. Another advantage to using the indenyl backbone structure is that the cyclopentadienyl complexes require large amounts of methyl-aluminum-hydride, a costly and toxic chemical, during the polymerization process; indenyl complexes may not have this requirement.





Results and discussion:

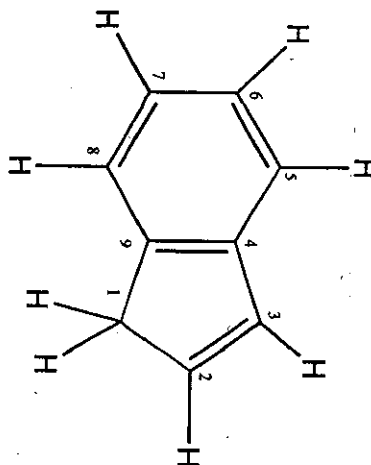
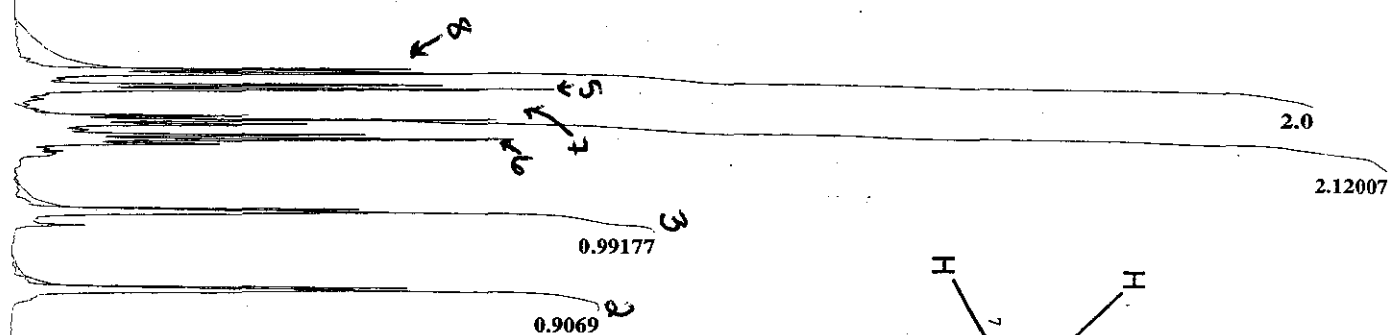
In order to monitor the products of the reactions, nuclear magnetic resonance (NMR) spectroscopy was used to gather information about the structure of the compounds based on the resonance of both the hydrogens (^1H NMR) and the carbons (^{13}C NMR) in the compound. The NMR spectra display the chemical shift, δ , on the x-axis in parts per million (ppm). The area under the peaks on the ^1H NMR can be integrated in order to relate the numbers of hydrogens responsible for each peak. The ^1H NMR and ^{13}C NMR data can be plotted against each other in a two-dimensional plot (HMQC) relating the each hydrogen to the carbon it is attached to.

Indene

The initial starting material for the synthesis of the catalyst precursor, was indene. The ^1H NMR spectrum of indene (Figure 4) has four peaks with a chemical shift downfield in the aromatic region of the spectrum ($\delta = 7.27, 7.35, 7.48, 7.55$); these peaks arise from the four hydrogens attached to the six-membered aromatic ring. A little further upfield there are two peaks ($\delta = 6.62, 6.97$) resulting from the two

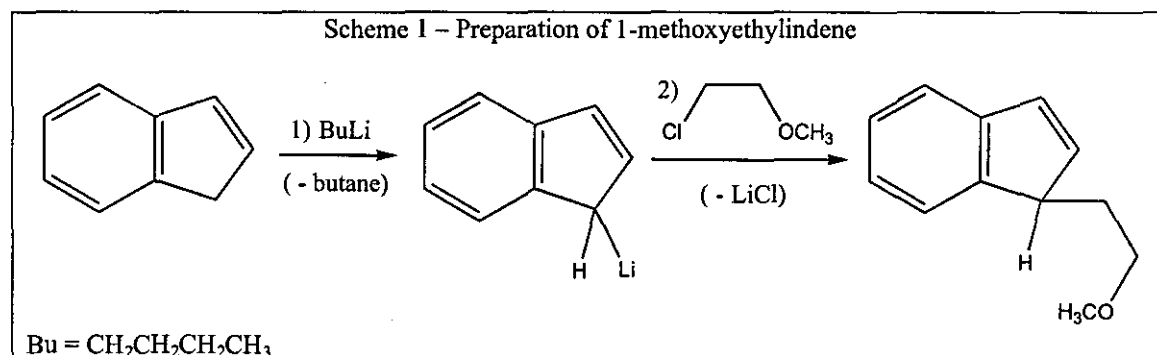
(Millions)

0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0 21.0



hydrogens adjacent to the double bond in the five-membered ring. Further upfield there is a single peak resulting from the two hydrogens attached to the same carbon on the five-membered ring ($\delta = 3.46$). There were several smaller peaks even farther upfield in the spectrum, but the integration shows that they were in such small quantities, that they were a result of impurities in the sample.

1-Methoxyethylindene

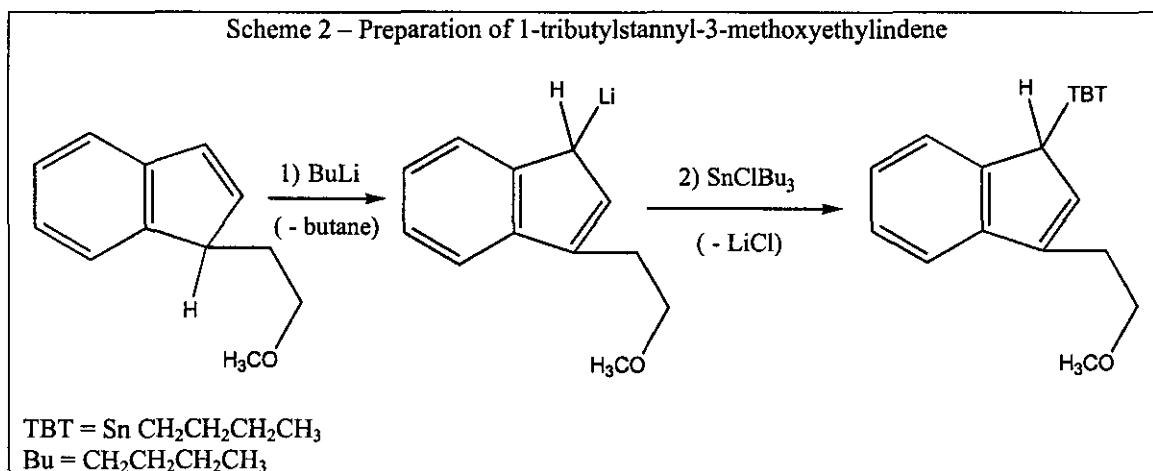


The indenyl complex that was synthesized had a 1-methoxy-ethyl pendant arm that was attached to the five-membered ring of the indenyl structure at the 1-position, and was also bonded from the oxygen to the titanium(IV). The purpose of this additional ligand is to hold the titanium(IV) group in proper orientation during the $\eta^5 \rightarrow \eta^3$ slippage that occurs in the polymerization process.

In order to attach the methoxy-ethyl pendant arm to the indene, purified indene was treated with butyllithium followed by 3-chloromethoxyethane (Scheme 1). The lithium was substituted for one of the hydrogens on the five-membered ring, which was then substituted for the methoxyethyl ligand; lithium chloride was a waste product of the reaction.

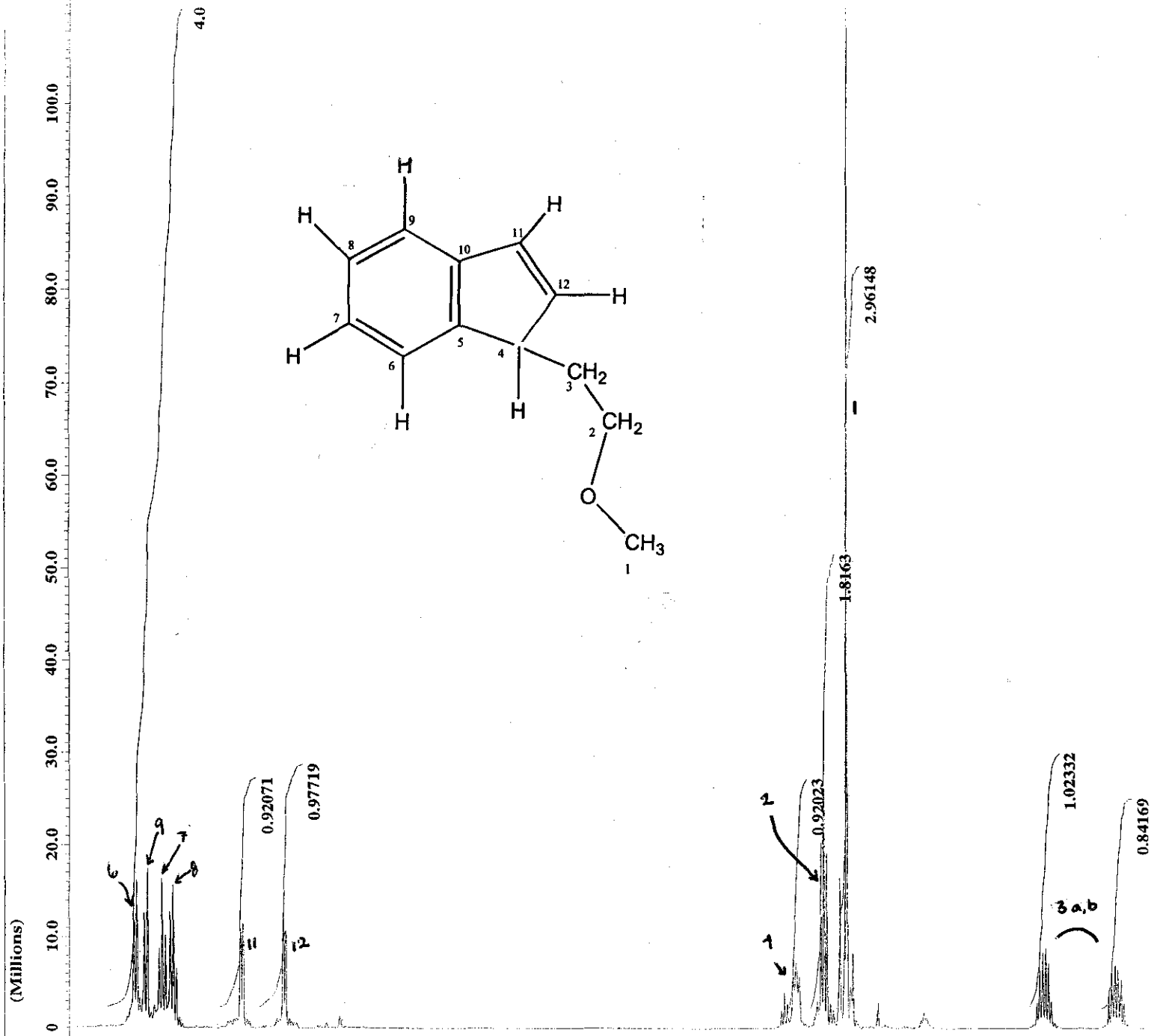
The ^1H NMR (Figure 5) of the product had the same six peaks in the region of $\delta = 6.7 - 7.6$, meaning that the indenyl structure remained static. The peak from the hydrogen adjacent to the methoxy-ethyl group was deshielded and shifted upfield ($\delta = 3.78$). There were several additional peaks from the methoxy-ethyl group: a peak from the methyl group, Hydrogen 1 (H1), at $\delta = 3.48$; a peak with an area of two hydrogens from H2 ($\delta = 3.61$); and two peaks from the hydrogens on Carbon 3 (C3) at $\delta = 1.92, 2.33$. The ^{13}C NMR spectrum (Figure 6) revealed that there were twelve different types of carbons in the compound. The HMQC (Figure 7) related the spectra to each other, verifying that the data had been correctly interpreted, and indicating that 1-methoxyethylindene was the product of this reaction.

1-Tributylstannyl-3-methoxyethylindene



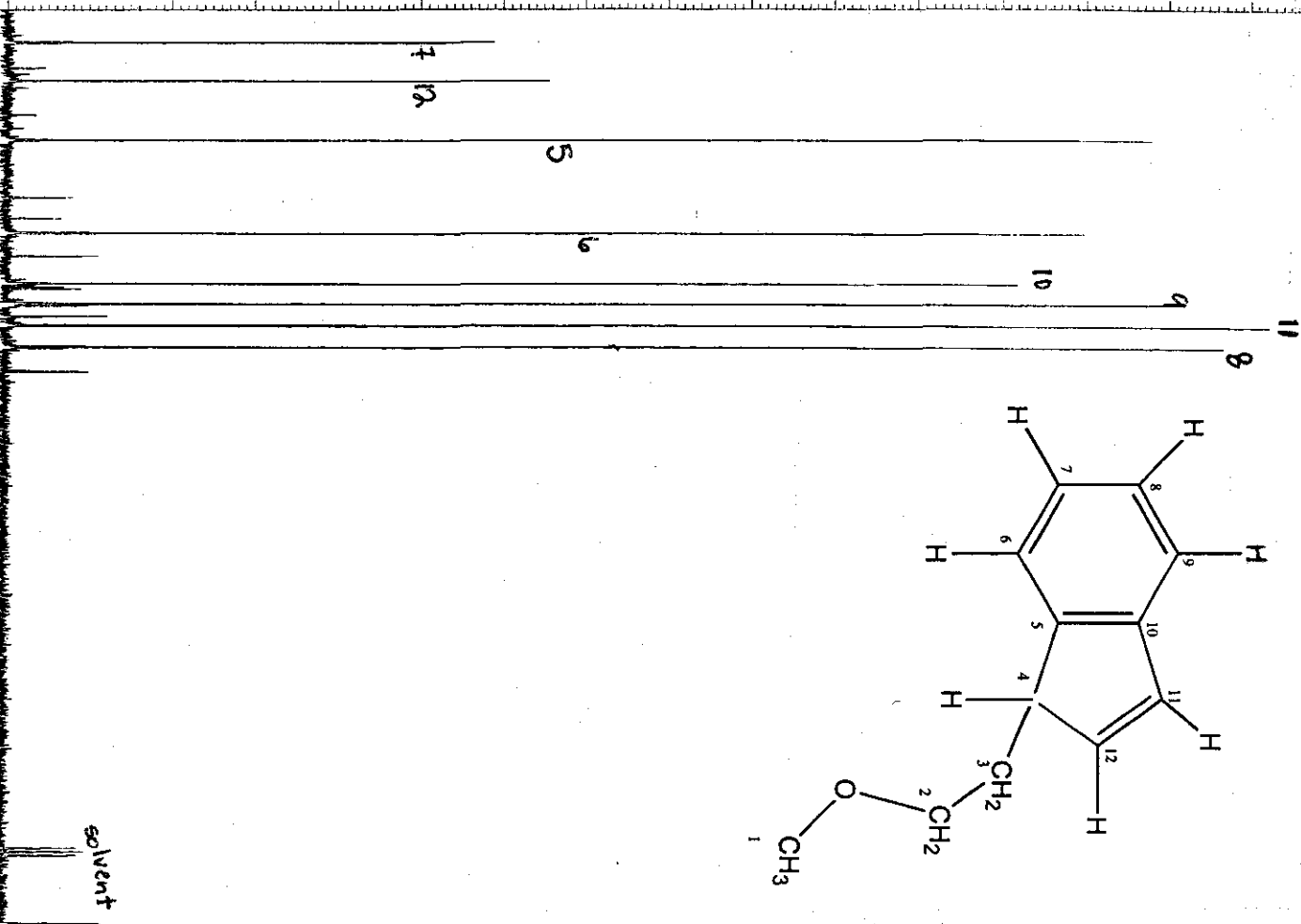
In order to form the complex between the titanium(IV) and the indenyl compound, the compound had to be converted to an indenyl transfer agent. In order to achieve this, a tributylstannyl agent was substituted for a hydrogen on the five-membered ring. This transfer agent was used because chlorotributylstannane is easily washed away from the product in most organic solvents. In order to add this ligand, the

Figure 5 - Integrated ^1H NMR - 1-methoxybicyclopentadiene



(Millions)

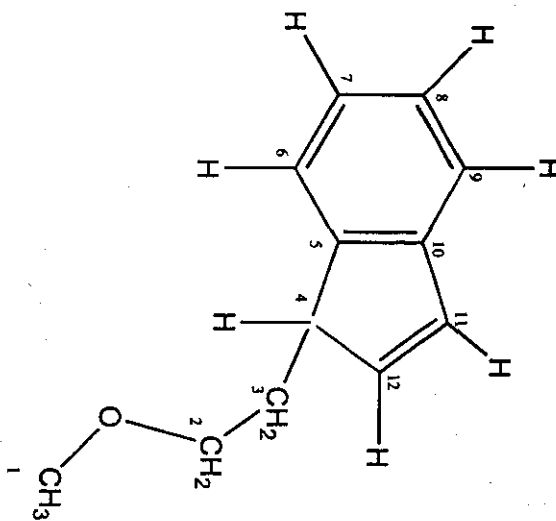
0 10.0 20.0 30.0 40.0 50.0 60.0 70.0 80.0 90.0 100.0 110.0 120.0 130.0 140.0 150.0



Y : parts per Million : ^{13}C

(Millions)

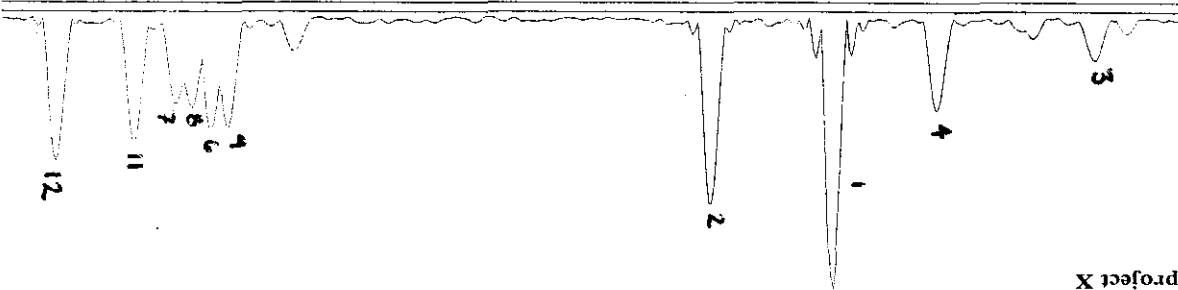
140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0



6 9 7 8 11 12

4 2

3 a,b



project X

1-methoxyethylindene was treated with butyllithium followed by chlorotributylstannane and lithium chloride was released (Scheme 2).

The HMQC of the product (Figure 8) revealed that there were an additional four different types of carbons added to the indenyl compound. The ^1H NMR showed that the four peaks from the hydrogens on the six-membered ring were still in the same location ($\delta = 7.15 - 7.65$), as well as the peak from H12 ($\delta = 6.52$). The shielding of H11 due to its proximity to the tributyltin ligand, caused it to shift significantly upfield ($\delta = 4.05$). There is no longer a hydrogen on C4, therefore there is no longer a peak for it on the ^1H NMR. The peaks that resulted from the resonance of H2 and H3 have both shifted slightly downfield due to the introduction of the adjacent double bond in the five-membered ring; the peak from H1 was not affected very strongly by the bond, and did not have a change in significant chemical shift.

The product had several additional peaks in the ethyl/methyl region of the spectrum from the tributyl groups. Integration of the ^1H NMR (Figure 9) indicated that there were 27 hydrogens responsible for these peaks, which is consistent with the number of hydrogens in three butyl groups.

2.3. *Trichloro (η^5 : η^1 methoxyethylindenyl) titanium(IV)*

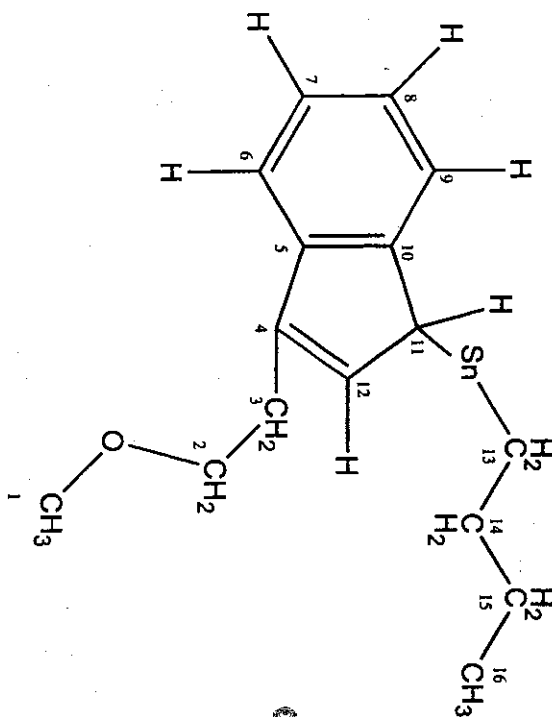
The 1-tributylstanny-3-methoxyethylindene was then reacted with titanium(IV)tetrachloride to obtain the final product (Scheme 3).

Y : parts per Million : ^{13}C

(Millions)

130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0

10.0 20.0



Solvent
6 9 7 8

12

11

2

3

14 15 16 13

Solvent

2

1

11

14 15 16 13

13

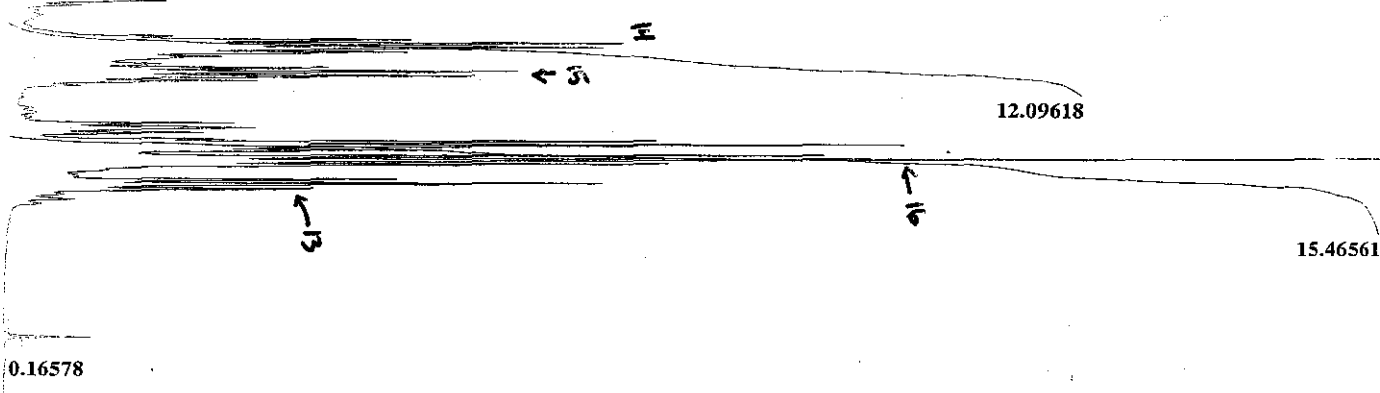
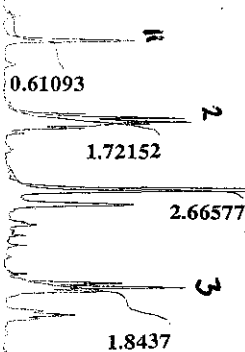
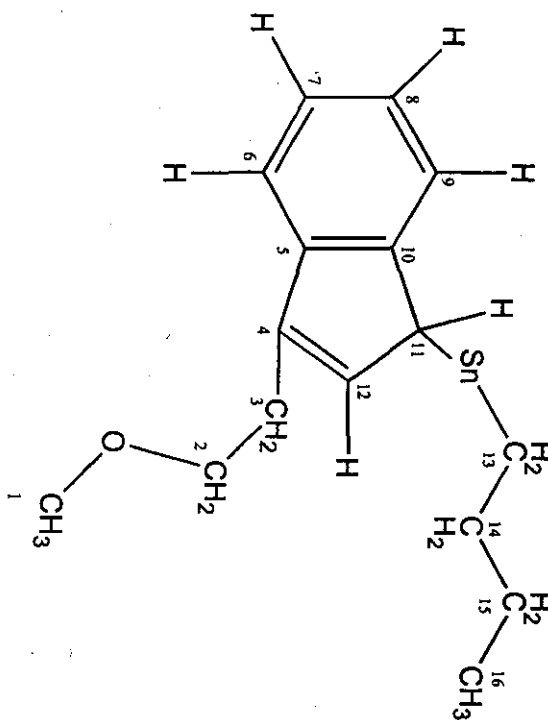
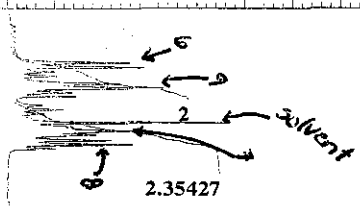
16

6 7 8 9

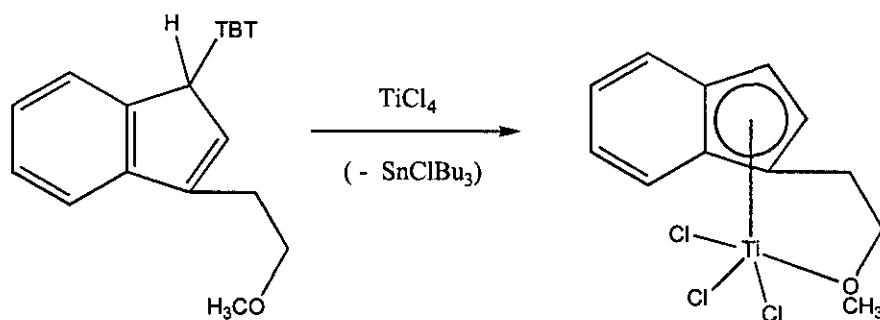
12

(Millions)

0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0 21.0 22.0 23.0 24.0 25.0 26.0 27.0 28.0



Scheme 3 – Preparation of trichloro (η^5 : η^1 methoxy-ethyl-indenyl) titanium(iv)

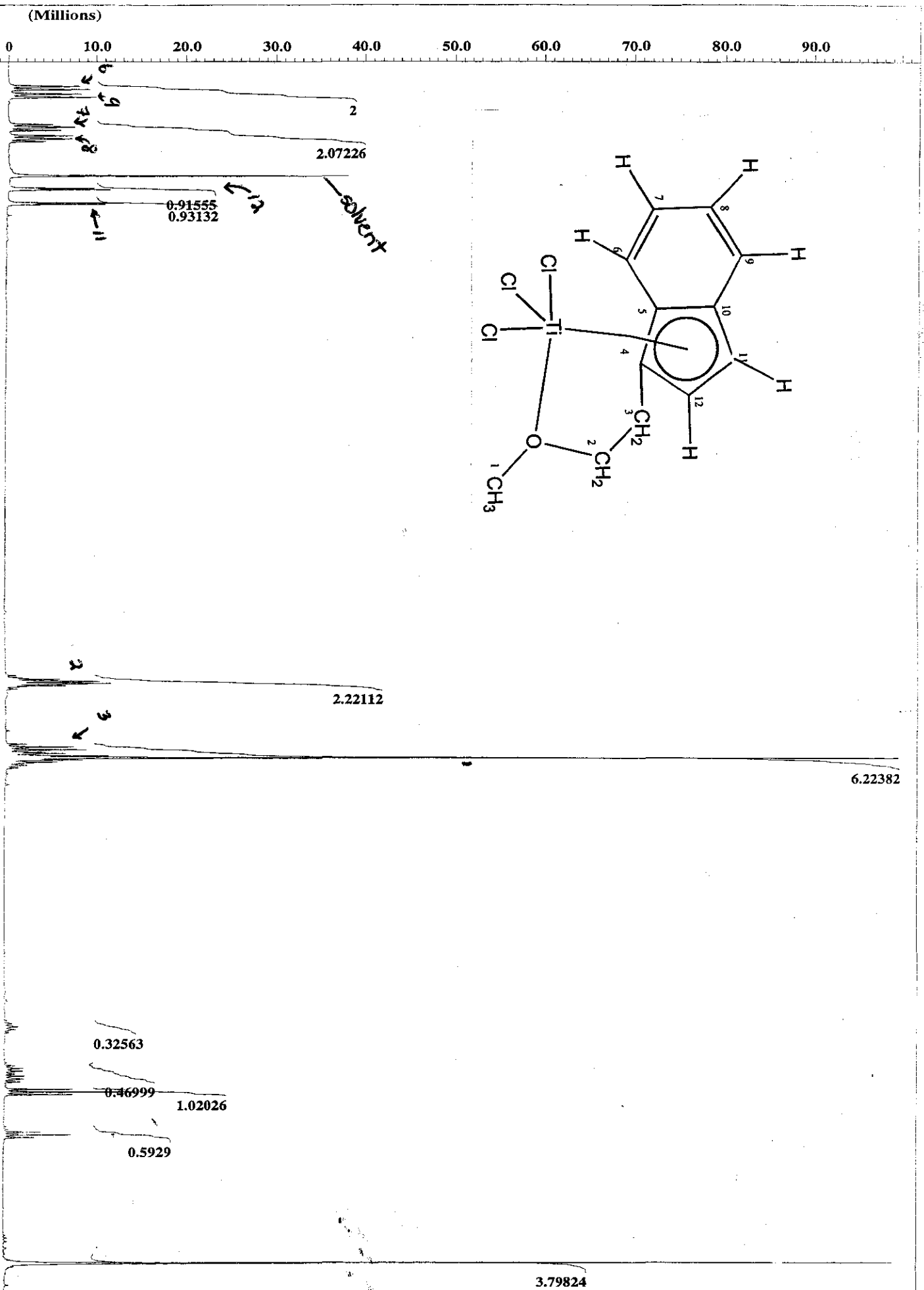


TBT = Sn CH₂CH₂CH₂CH₃

Bu = CH₂CH₂CH₂CH₃

The ^1H NMR (Figure 10) of the product indicated that H11 had shifted back downfield ($\delta = 7.06$) and C11 also shifted downfield to the aromatic region of the ^{13}C ($\delta = 124$) spectrum as a result of the aromatization of the five-membered ring; H12 also shifted slightly downfield ($\delta = 7.1$) for the same reason. The other four aromatic peaks ($\delta = 7.49 - 7.84$) are still present on the spectrum. As a result of the aromatization of the five-membered ring, the peak from the resonance of H3 had shifted downfield ($\delta = 3.46$), and combined with the peak from H1 ($\delta = 3.42$); H2 has shifted only slightly downfield ($\delta = 3.90$). There are several small peaks from residual chlorotributylstannane that was not washed away from the product. The integration confirmed that the peaks were the result of only a tiny amount of hydrogen, indicating that it was not part of the structure of the compound. There was also a large peak at $\delta = 0.06$ caused by joint grease that was introduced into the sample as an impurity during the reaction. The HMQC of this compound (Figure 11) indicated that there were eleven different types of carbons. Although C7 and C8 are not completely identical, the two-dimensional plot confirmed that both of these atoms have the same chemical shift in the ^{13}C spectrum ($\delta = 129$). All

Figure 10 - Integrated ¹H NMR - trichloro (η⁵-methoxyethylindenyl) titanium(IV)

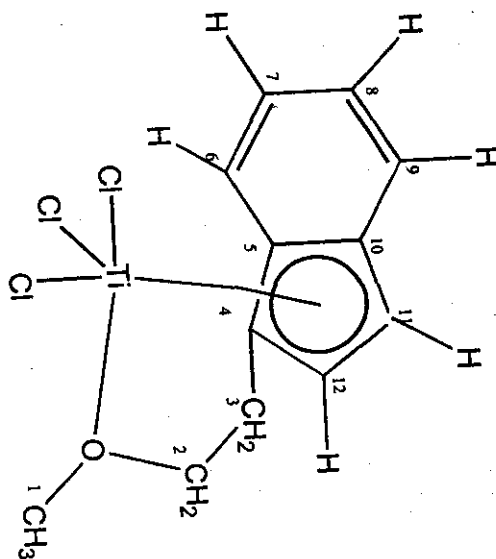


Y : parts per Million : ^{13}C

140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0

(Millions)

10.0 40.0 70.0



69 12 11 solvent

2 3 1

Solvent

12

11

10

9

8

7

6

2

1

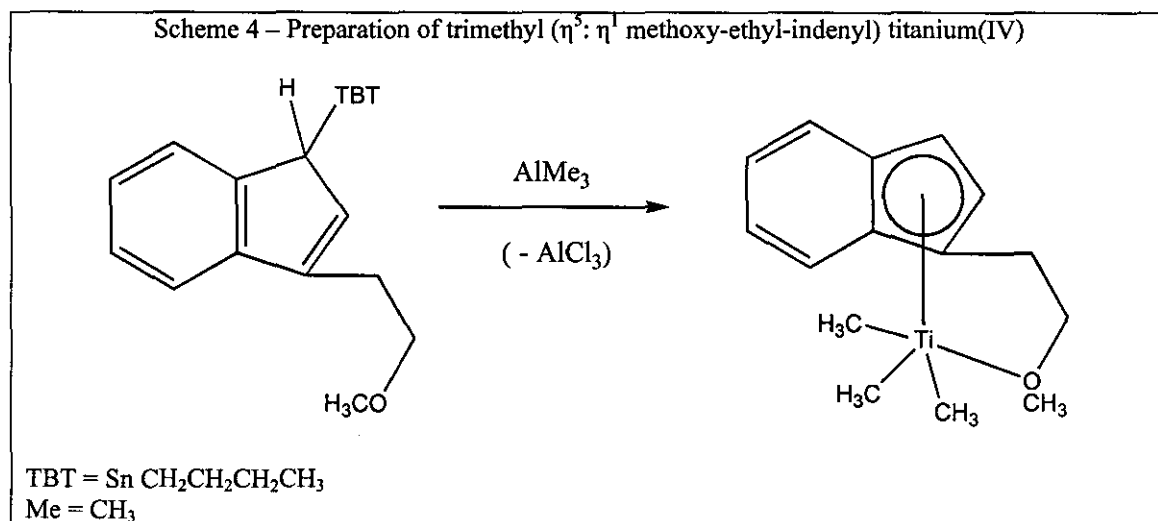
3

12 11 10 9 8 7 6 5 4

of the data collected is consistent with the formation of the final product, trichloro (η^5 : η^1 methoxyethylindenyl) titanium(iv) complex.

2.4. Trimethyl (η^5 : η^1 methoxyethylindenyl) titanium(iv)

In order to function as a polymerization catalyst, the trichloro (η^5 : η^1 methoxyethylindenyl) titanium(IV) must have the chlorine atoms replaced by methyl groups. In order to achieve this, the compound will be treated with trimethylaluminum (Scheme 4). Once this reaction has been completed, the catalyst will be complete, and can be then be tested for its effectiveness in polymerizing olefins.



Experimental:

All procedures were carried using standard Schlenk techniques under argon flow or vacuum, or in an argon filled dry-box. The solvent that were used, methylene dichloride, hexane, and ethyl ether, had a minute water content, and were degassed immediately prior to use. The NMR solvent that was used for all of the spectroscopy was chloroform-d dried with sodium metal and distilled under vacuum.

The preparations of 1-methoxy-ethyl-indene, and 1-tributylstannyl-3-methoxy-ethyl-indene were performed by prior students working on this project and these compounds were used as received.

Preparation of trimethyl (η^5 : η^1 methoxyethylindenyl) titanium(IV):

In a 100-mL round-bottom Schlenk flask containing a magnetic stir bar, titanium(IV) tetrachloride (8.1 mL of 1.0M solution, 0.00810 moles) was combined with degassed methylene dichloride (25 mL). In 100-mL Schlenk tube, 1-tributylstanny-3-methoxyethylindene (3.6 grams, 0.00803 moles) was dissolved in degassed methylene dichloride (25 mL). This solution was then added dropwise to the flask containing the titanium(IV) tetrachloride via cannula, while it was stirred continuously. As the titanium(IV) tetrachloride was added, the solution slowly turned from a pale yellow to red. The solution was stirred for 12 hours while the reaction proceeded.

The product of the reaction was a dark purple solid, in a bright red liquid. The liquid was filtered out, and the solid product was vacuumed dry for five hours. In order to re-crystallize the product, it was dissolved in degassed ethyl ether (50 mL) and stirred for 2 hours. The red liquid was then filtered via cannula into a small Schlenk tube. This solution was then concentrated by vacuuming away the solvent until a supersaturated solution had been obtained. A solution that is supersaturated at room temperature will become oversaturated at low temperatures, and the solute will not be as soluble in the solvent causing crystals to fall out of solution. The supersaturated solution was placed in the freezer for 48 hours to allow the crystals to grow.

When the Schlenk tube was removed from the freezer, the liquid was immediately transferred via cannula into a second Schlenk tube, and the process was repeated to grow

a second batch of crystals. The first batch of crystals were vacuumed dry for 3 hours to remove any remaining ethyl ether. Once the crystals were completely dry, they were dissolved in chloroform-d, and NMR spectroscopy was performed on the compound.